



Selenite-catalyzed oxidative carbonylation of alcohols to dialkyl carbonates

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ABSTRACT

The oxidative carbonylation of alcohols to prepare corresponding dialkyl carbonates was investigated using alkali metal methylselenite ($\text{MSeO}_2(\text{OCH}_3)$) and alkali metal selenite (M_2SeO_3 , $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Cs}$) as catalysts. Of various alcohols tested, methanol and 2-methoxyethanol (MEG) are found to be highly reactive, affording corresponding dialkyl carbonates in yields of more than 30%, which are significantly higher than those achieved with Cu-based catalysts under similar reaction conditions. XRD and GC-Mass analysis of the spent catalyst recovered from the M_2SeO_3 -catalyzed reaction of methanol revealed that M_2SeO_3 was converted into elemental selenium and MHCO_3 along with the formation of several selenium-containing by-products including malodorous dimethyldiselenide, 1,2-dimethoxydiselane, and O_2Se -dimethyl carbonoselenoate. On the contrary, the oxidative carbonylation of MEG with K_2SeO_3 was highly selective toward the formation of bis(2-methoxyethyl) carbonate (BMEC), without producing any selenium-containing by-products. A plausible mechanism for the $\text{MSeO}_2(\text{OCH}_3)$ - and M_2SeO_3 -catalyzed oxidative carbonylation of MEG was suggested on the basis of mechanistic and experimental results.

1. Introduction

Dialkyl carbonates (DACs) have attracted much attention due to their environmentally benign characteristics and versatile applications such as aprotic solvents [1], monomers for polycarbonates [2], polyurethanes [3], and utility as alkylating agents [4]. Dialkyl carbonates also find uses as electrolyte solvents [5] and gasoline additives [6]. Dialkyl carbonates can be easily prepared by the reactions of alcohols with phosgene [7]. However, such phosgenation reactions possess inherent drawbacks arising from the use of highly toxic phosgene [8]. As alternatives to the phosgenation reaction, several processes have been developed including transesterification [9], methyl nitrile carbonylation [10,11], alcoholysis of urea [12], oxidative carbonylation [13–15], and carboxylation [16–22]. Among these, the synthesis of DACs from the carboxylation by CO_2 would be most desirable from environmental and economic points of view. Unfortunately, economically viable carboxylation processes utilizing CO_2 as a raw material have not developed yet. Unlike the carboxylation process, oxidative carbonylation processes to produce dimethyl carbonate using a copper-based catalyst like CuCl have been commercialized by Enichem [23]. Since then, much effort has been devoted to enhance the activity of Cu-based catalysts.

One successful example is the use of PdCl_2 and an ammonium salt along with CuCl . The Dow chemical company has also issued several patents [24–26] on the use of activated carbon-supported copper catalysts. Nonetheless, the catalytic systems so far reported for oxidative carbonylation reactions still need improvement, especially in terms of the activity, stability, recovery, and corrosivity of catalysts.

To circumvent the problems associated with the use of Cl-containing catalysts, much effort has been made to develop high-performance Cu-based catalysts without possessing a halide ligand or ligands for the oxidative carbonylation of methanol to produce DMC. As a result, significant advances have been achieved on the synthesis of Cl-free Cu-based catalysts (Cu/AC) as well as on the improvement of their catalytic activities [27–31]. For instance, Li et al. have shown demonstrated that the activity and stability of Cu/AC can be enhanced to a great extent by controlling the size and distribution of Cu species, as well as by modifying the oxidation state of Cu and the type of surface oxygenated species [29,28–31].

As an alternative to Cu-based catalysis, selenium metal-catalyzed oxidative carbonylation of amines to substituted ureas and carbamates has been reported [32]. The driving force for the oxidative carbonylation is the formation of carbonyl selenide (SeCO). Due to a weak π - π

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interaction, nucleophiles like amines are able to attack the carbonyl carbon atom of SeCO. In another study, dialkyl carbonates were synthesized using elemental selenium as the catalyst, but only in the presence of large amounts strongly basic alkali metal alkoxides [33]. Catalytic systems comprising elemental selenium and an inorganic base have been used in the synthesis of glycerol carbonate by oxidative carbonylation of glycerol. Here, the base was used to enhance the nucleophilicity of glycerol to interact with SeCO [34].

In this context, we have previously reported that potassium selenite (K_2SeO_3), potassium methylselenite, and dialkylimidazolium methylselenites are highly effective catalysts for the oxidative carbonylation of aromatic amines in alcohols, producing corresponding substituted ureas and carbamates in moderate to excellent yields depending on the catalyst employed [35]. However, such selenite compounds have never been employed as catalysts for the synthesis of dialkyl carbonates through the oxidative carbonylation of alcohols.

In this work, we report on the catalytic activities of alkali metal selenites for the oxidative carbonylation of alcohols including methanol and ethylene glycol monomethyl ether (MEG). A plausible pathway leading to the formation of dialkyl carbonates is also discussed on the basis of experimental, X-ray diffraction, and gas chromatography–mass spectrometry (GC-Mass) results.

2. Experimental

2.1. Materials

All chemicals including alcohols and catalysts used for the synthesis of dialkyl carbonates were purchased from Aldrich Chemical Co. CO and O₂ with a purity of 99.9% each were obtained from Shin Yang Gas Co. Korea. All catalysts were dried under vacuum prior to use. Alkali metal methylselenites were synthesized according to a previously reported procedure [35].

Synthesis of alkali metal methylselenite. In a 100-mL 3-necked flask equipped with a reflux condenser, alkali metal carbonate (M₂CO₃, M = Li, Na, K, Cs; 15 mmol) was reacted with two equivalents of SeO₂ (3.3 g, 30 mmol) in methanol (30 mL) at room temperature for 2 h. After the completion of the reaction, ethyl acetate was added to the reaction mixture to precipitate white solid. The resulting precipitates were collected by filtration and dried under vacuum to give MSeO₂(OCH₃) in yield of 90 ~ 95%.

2.2. Instrumentation

Analysis of liquid products obtained from the oxidative carbonylation reactions was performed using an Agilent 6890 gas chromatograph (GC) equipped with a flame ionization detector (FID) and a DB-5 capillary column as well as using 400 MHz Bruker NMR spectrometer and an Agilent 6890-5973 MSD GC-Mass spectrometer provided with a HP-MS capillary column. The XRD patterns of fresh and spent selenium catalysts were obtained using a Shimadzu X-ray diffractometer (XRD-6000) using nickel-filtered $CuK\alpha$ radiation with a 2θ angle from 10 to 90°. FT-IR spectra were obtained using a Nicolet FT-IR spectrometer (iS10, USA) equipped with a SMART MIRACLE accessory.

2.3. Oxidative carbonylation reaction

All experiments were conducted in a 25 mL stainless steel reactor equipped with a magnetic stirrer, a thermocouple, and an electric heater. The reactor was loaded with an appropriate alcohol and a catalyst. The reactor was pressurized to 2.0 MPa with a mixed gas of CO/O₂ (v/v = 80/20) at room temperature and then heated to desired temperatures with vigorous stirring. The reactor was further pressurized to 5.0 MPa at the specified temperature and then maintained constant throughout the reaction using a gas reservoir equipped with a high pressure regulator and a pressure transducer. At the end of the

reaction, the reactor was cooled to room temperature. The yields and selectivities of dialkyl carbonates, and the conversions of alcohols were obtained by GC and then confirmed by ¹H NMR analysis using 1,4-dioxane as an internal standard (Supplementary data, Figs. S-1 and S-2). Comparison of the fresh and spent catalysts was made by means of FT-IR and XRD. It should be noted that malodorous dimethyl selenide could be produced as a by-product in some of these reactions and thus the reaction workup should be carried out in a well-ventilated fume hood.

The conversion of an alcohol and the yield and selectivity of DAC were calculated by the following formulas:

$$\text{Alcohol conversion (\%)} = [(\text{moles of alcohol reacted})/(\text{moles of starting alcohol})] \times 100\% \quad (1)$$

$$\text{DAC yield (\%)} = [2(\text{moles of DAC})/(\text{moles of starting alcohol})] \times 100\% \quad (2)$$

$$\text{Selectivity (\%)} = [2(\text{moles of DAC})/(\text{moles of alcohol converted})] \times 100\% \quad (3)$$

3. Results and discussion

3.1. Catalytic performances of various catalysts

The synthesis of DMC from the oxidative carbonylation of methanol was investigated in the presence of K_2SeO_3 or Na_2SeO_3 . As shown in Table 1, K_2SeO_3 produced DMC in yield of 28.1% (entry 3) along with the formation of small amounts of side products such as dimethyl ether (DME) and Se-containing organic compounds when the oxidative carbonylation reaction of methanol was conducted at 70 °C with the $CH_3OH/[Se]$ molar ratio of 30. This is a rather surprising result considering that the yield of DMC using Cu-based catalysts is almost negligible under the same experimental condition (entries 15 and 16). Interestingly, dimethoxymethane (DMM) and methylformate (MF) were not produced in the Se-catalyzed oxidative carbonylation of methanol, although DMM and MF are side products frequently observed in the Cu-catalyzed carbonylation reaction. Instead, the formation of small amounts of selenium-containing side products were observed (*vide infra*).

Being motivated by this result, the activities of various alkali metal selenites (M₂SeO₃) and alkali metal methylselenites [MSeO₂(OCH₃)]⁺, M = Li, Na, K, and Cs) were evaluated for the synthesis of DMC via oxidative carbonylation of methanol. In general, as shown in Table 1, alkali metal methylselenites exhibited lower activities than the corresponding alkali metal selenites. Nonetheless, in some case, the use of an alkali metal methylselenite could be more desirable especially in the synthesis of a supported Se catalyst because it is very soluble in methanol. The activity of an alkali metal selenite is strongly affected by the variation of alkali metal ion and reaction temperature. For instance, K_2SeO_3 , Cs_2SeO_3 produced DMC in yields around 28 ~ 29% at 70 °C (entries 3 and 4). By contrast, the oxidative carbonylation of methanol in the presence of Li_2SeO_3 or Na_2SeO_3 did not take place at 70 °C (entries 1 and 2). Surprisingly, Li_2SeO_3 and Na_2SeO_3 afforded DMC in yield of 33.0 and 32.9%, respectively when the temperature increased to 100 °C. Similar trends were observed in the alkali metal methylselenite-catalyzed carbonylation reactions to produce DMC. However, contrary to our expectation, the yield of DMC was negligible when $CsSeO_2(OCH_3)$ was used as a catalyst (entry 8). The reason is not clear at the moment, but it is likely that, for some reason, the transformation of $CsSeO_2(OCH_3)$ into an active species is prohibited (*vide infra*).

It has been reported that, in the oxidative carbonylation reactions of amines using imidazolium-based alkylselenite catalysts, the first step is the reduction of Se (IV) by CO [36]. Likewise, the reduction of Se (IV) to Se (II) or Se (0) is expected to occur first in the selenite-catalyzed oxidative carbonylation of methanol. If this is the case, the Se = O

Table 1Catalytic performance of various Se- and Cu-based catalysts for the oxidative carbonylation of methanol^a.

Entry	Catalyst	Conversion (%)		DMC Yield (%)		Selectivity (%) DMC/DME ^b /Others	
		70 °C	100 °C	70 °C	100 °C	70 °C	100 °C
1	Li ₂ SeO ₃	0	34.4	0	33.0	–	96.8/2.0/1.2
2	Na ₂ SeO ₃	0	35.6	0	32.9	–	92.4/4.2/3.4
3	K ₂ SeO ₃	31.0	25.6	28.1	22.5	90.6/7.1/2.3	87.9/8.3/3.8
4	Cs ₂ SeO ₃	31.5	24.4	29.4	21.2	93.3/5.4/1.3	86.9/8.8/4.3
5	LiSeO ₂ (OCH ₃)	0	33.4	0	30.7	–	91.9/5.4/2.7
6	NaSeO ₂ (OCH ₃)	0	31.7	0	28.8	–	90.9/5.0/4.1
7	KSeO ₂ (OCH ₃)	25.7	22.1	22.0	18.6	85.6/10.1/4.3	84.3/11.3/4.4
8	CsSeO ₂ (OCH ₃)	1.0	18.1	1.0	17.2	100/0/0	95.0/2.9/2.1
9 ^c	Se/KHCO ₃	15.5	22.3	14.4	19.9	92.9/4.5/2.6	89.2/6.3/4.5
10 ^d	Se/KHCO ₃	18.1	24.2	16.9	21.3	93.3/4.3/2.4	88.0/5.8/4.1
11 ^c	Se/K ₂ CO ₃	7.6	18.7	7.3	16.7	96.1/2.6/1.3	89.3/6.7/4.0
12	Se/NaHCO ₃	0	24.9	0	22.5	–	90.4/6.4/4.2
13	Se	0	0	0	0	–	–
14	KHCO ₃	0	0	0	0	–	–
15	CuCl ₂	5.8	21.9	4.1	19.5	70.7/27.6/1.7	89.0/8.6/2.4
16 ^e	Cu/Pd/N	3.1	22.8	2.0	19.9	64.5/32.3/3.2	87.2/9.5/3.3

^a Conditions: MeOH (150 mmol), P = 5 MPa (O₂/CO = 1/4), t = 2 h. [Se] = 5 mmol, [Cu] = 5 mmol.^b DME: dimethyl ether.^c Molar ratio of Se/K = 1/2.^d Se/KHCO₃ was ground before use.^e Cu/Pd/N = Cu(OMe)₂/PdCl₂(PPh₃)₂/NMe₄Cl, Molar ratio of Cu/Pd/N = 5/0.1/5.

bonds of Na₂SeO₃ and NaSeO₂(OCH₃) should be much stronger than those of K₂SeO₃ and KSeO₂(OCH₃), thereby preventing the cleavage of Se = O bond by CO. This is reasonable in consideration of the Lewis acidity and the size of the alkali metal ion. As Na⁺ is more Lewis acidic than K⁺, it is assumed that Na⁺ interacts more strongly with the basic selenite anions, thereby suppressing the reduction of Se (IV) by CO. It is likely that there is a subtle balance between the activity of alkali metal selenite and cation-anion interaction. One common phenomenon observed in the selenite-catalyzed oxidative carbonylation of methanol is that a number of methanol-soluble selenium-containing species are produced along with the generation of insoluble grayish black precipitates.

3.2. Catalyst characterization

To understand the catalytic nature of alkali metal selenites, XRD analysis was performed with fresh and spent catalysts. For this purpose, oxidative carbonylation of methanol was carried out at 70 °C for 2 h in the presence of K₂SeO₃ with a CH₃OH/Se molar ratio of 30. After reacting for 2 h, a grayish black solid precipitate was collected by filtration, washed with CH₃OH, and dried under vacuum at room temperature. As shown in Fig. 1c, XRD analysis showed that the solid consisted of mostly potassium bicarbonate (KHCO₃) and elemental selenium. A similar trend was also observed for the oxidative carbonylation of methanol with the presence of Cs₂SeO₃ (Supplementary Information, Fig. S-4). However, there is a possibility that other species different from K₂SeO₃, Se, and KHCO₃ could be present in the solid if they are in a highly dispersed or amorphous state. Similar XRD patterns were also obtained from the oxidative carbonylation of methanol at 70 °C with KSeO₂(OCH₃) (Fig. 1d). As expected from the negligible activities of Na₂SeO₃ and CsSeO₂(OCH₃) at 70 °C for the carbonylation of methanol, they were recovered unchanged after the reaction. As shown in Fig. 2d and e, the XRD patterns of the used catalysts were almost same as those of the fresh ones. Any sign of the formation of elemental selenium was not observed.

The formation of Se and KHCO₃ from K₂SeO₃, and the possible presence of other Se- and K-containing species in the solid mixture were further investigated by FT-IR spectroscopy. As shown in Fig. 3, the FT-IR spectrum of the solid precipitates clearly reveals that KHCO₃ is the only IR-active species, supporting the complete transformation of

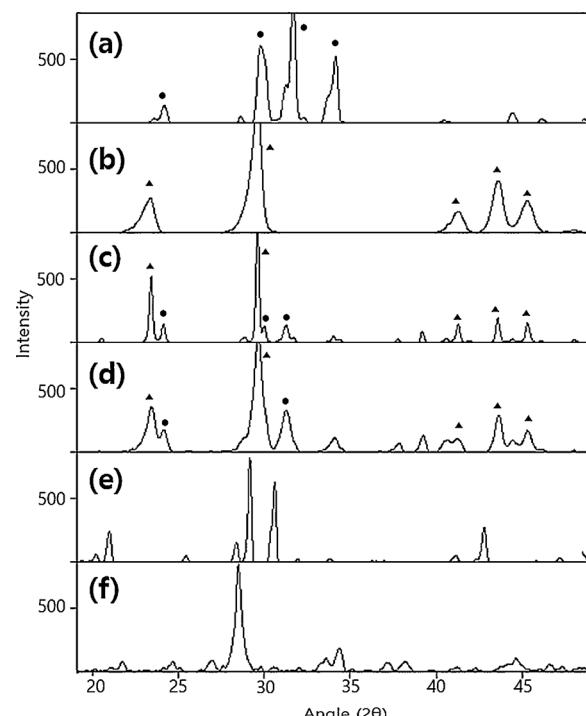


Fig. 1. XRD patterns: (a) KHCO₃ (●), (b) selenium (▲), (c) recovered solid from the K₂SeO₃-catalyzed oxidative carbonylation of methanol at 70 °C, and (d) recovered solid from the KSeO₂(OCH₃)-catalyzed oxidative carbonylation of methanol at 70 °C, (e) Fresh K₂SeO₃, and (f) Fresh KSeO₂(OCH₃).

K₂SeO₃ into Se and KHCO₃. The presence of other IR-active species different from KHCO₃ was not observed. The absorption peak appeared at 1624 cm⁻¹ can be attributed to the C=O stretching mode. In addition, the two peaks observed at 1389 and 1362 cm⁻¹ have been assigned to the coupled vibrations between the O—H···O in-plane bending and the CC=OO stretching modes, respectively. The two peaks appearing at 1004 and 976 cm⁻¹ can be associated with the C—O stretching coupling with the CC=OO stretching mode and the O—H···O out-of-plane bending mode, respectively [37].

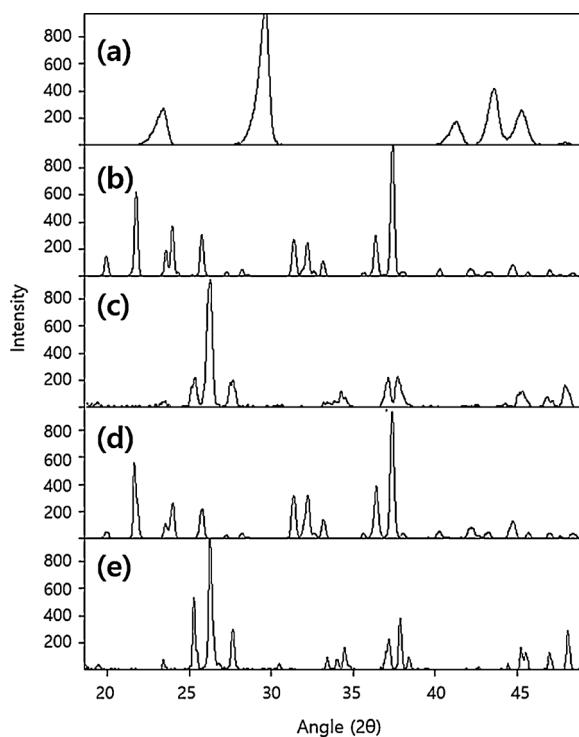


Fig. 2. XRD patterns: (a) Se, (b) Na_2SeO_3 , (c) Fresh $\text{CsSeO}_2(\text{OCH}_3)$, (d) recovered solid from the Na_2SeO_3 -catalyzed oxidative carbonylation of methanol at 70°C , and (e) recovered solid from the $\text{CsSeO}_2(\text{OCH}_3)$ -catalyzed oxidative carbonylation of methanol at 70°C .

The formation of elemental selenium and KHCO_3 from both K_2SeO_3 and $\text{KSeO}_2(\text{OCH}_3)$ suggests that Se (IV) species are reduced to Se(0), accompanying the formation of KHCO_3 during the carbonylation. On the contrary, Na_2SeO_3 was completely inactive at 70°C (entry 2 in Table 1). As can be conceivable from the negligible activity of Na_2SeO_3 at 70°C , Na_2SeO_3 was recovered unchanged after oxidative carbonylation (Fig. 2b and d). Na_2SeO_3 , however, became active at an elevated temperature of 100°C (entry 2 in Table 1). Characterization of the solid precipitates recovered from the carbonylation at 100°C revealed that Na_2SeO_3 was converted into a mixture of elemental selenium and NaHCO_3 , consistent with the precipitates formed by K_2SeO_3 and

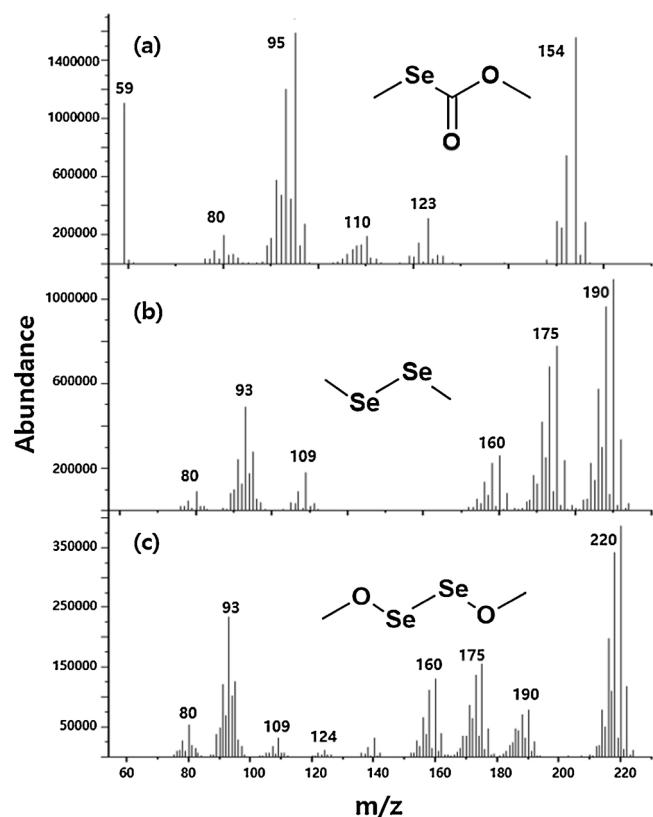


Fig. 4. Mass spectra of selenium-containing side products observed from the carbonylation of methanol in the presence of K_2SeO_3 : (a) $\text{CH}_3\text{SeCO}_2\text{CH}_3$, (b) $(\text{CH}_3\text{Se})_2$, and (c) $(\text{CH}_3\text{OSe})_2$.

$\text{KSeO}_2(\text{OCH}_3)$ at 70°C (Supplementary Information, Fig. S-3).

One noteworthy drawback in the selenite-catalyzed oxidative carbonylation of methanol is the formation of various malodorous organo-selenium by-products, which constitute a major inconvenience when this reaction is carried out. In order to identify those by-products, oxidative carbonylation was carried out with K_2SeO_3 at 70°C for 2 h, and insoluble solids were removed by filtration as usual. GC-Mass analysis of the remaining solution revealed that at least three selenium containing species were produced, including $(\text{CH}_3\text{Se})_2$ (dimethyl

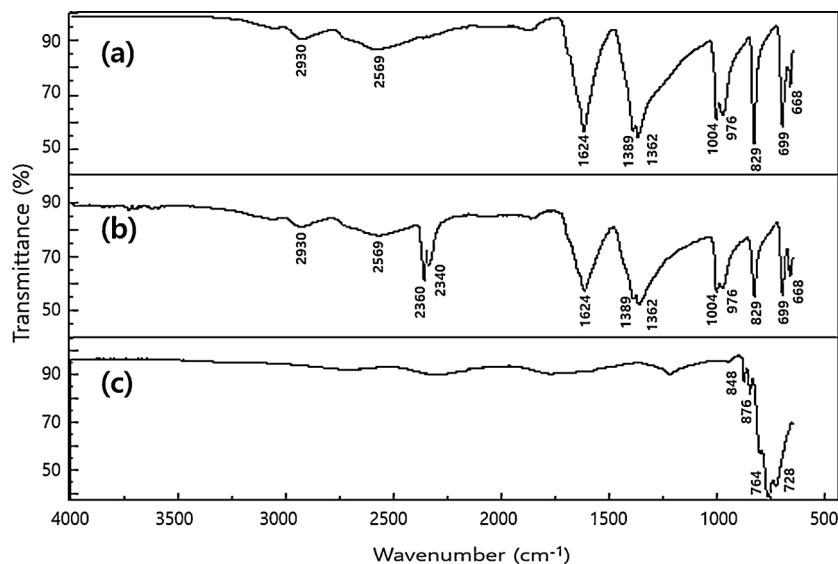


Fig. 3. FT-IR spectra of (a) the solid precipitates recovered from the oxidative carbonylation of methanol conducted at 70°C for 2 h in the presence of K_2SeO_3 , (b) K_2CO_3 and (c) Fresh K_2SeO_3 . The molar ratio of methanol/ K_2SeO_3 was set at 30 in the carbonylation.

Table 2
Oxidative carbonylation reaction of different alcohols^a.

Entry	Alcohol	Catalyst	DAC Yield (%) ^b	pKa (ref.) ^c
1	Methanol	K ₂ SeO ₃	28.1	15.5 ([38])
2	Ethanol	K ₂ SeO ₃	8.4	15.9 ([38])
3	1-Propanol	K ₂ SeO ₃	2.8	16.1 ([39])
4	1-Butanol	K ₂ SeO ₃	1.1	16.1 ([39])
5	2-Chloroethanol	K ₂ SeO ₃	0	14.3 ([40])
6	2,2,2-Trifluoroethanol	K ₂ SeO ₃	0	12.5 ([38])
7	Phenol	K ₂ SeO ₃	< 1 ^d	9.9 ([39])
8	MEG ^e	K ₂ SeO ₃	29.6	14.8 ([39])
9 ^f	MEG	Se/KHCO ₃	27.9	–
10 ^g	MEG	Se/KHCO ₃	32.4	–
11	MEG	CuCl ₂	4.1	–
12 ^h	MEG	Cu/Pd/N	1.8	–

^a Conditions: alcohol (150 mmol), K₂SeO₃ (5 mmol), P = 5 MPa (O₂/CO = 1/4), t = 2 h.

^b DAC: dialkyl carbonate.

^c Reference No.

^d Diphenyl carbonate yield was less than 1% at 180 °C.

^e MEG: 2-methoxyethanol.

^f Molar ratio of Se/K = 1/2.

^g Se/KHCO₃ was ground before use.

^h Cu/Pd/N = Cu(OMe)₂/PdCl₂(PPh₃)₂/NMe₄Cl, Molar ratio of Cu/Pd/N = 5/0.1/5.

diselenide or 1,2-dimethyldiselenane), CH₃SeCO₂CH₃ (O,Se-dimethyl carbonoselenoate), and (CH₃OSe)₂ (1,2-dimethoxydiselenane) (Fig. 4). A mechanism for the formation of the Se-containing by-products was proposed in the Supplementary data (Scheme S-1). The above three selenium species were also observed in the Na₂SeO₃-catalyzed oxidative carbonylation of methanol at the elevated temperature of 100 °C. Of the three selenium-containing species, dimethyl diselenide was found to be largely responsible for the foul odor observed from the product mixture.

3.3. Effect of alcohol

In order to investigate the applicability of this reaction to different alcohols, reactions were carried out using a variety of alcohols in place of methanol. Volatile selenium compounds are well known for being malodorous, and the generation of volatile dimethyl diselenide as a by-product during the oxidative carbonylation of methanol was a significant inconvenience. Therefore, an additional aim was to mitigate the generation of malodorous selenium species by using alcohols with lower volatility. To this end, oxidative carbonylation reactions were conducted at 70 °C using different alcohols in the presence of K₂SeO₃ as the catalyst. As listed in Table 2, the carbonylation in different alcohols afforded corresponding dialkyl carbonates, but the yields of dialkyl carbonates varied significantly with the alcohol employed. The activity of K₂SeO₃ for the carbonylation of C₂–C₄ alcohols including ethanol, 1-propanol, and 1-butanol are much lower than that of methanol, producing corresponding dialkyl carbonates in poor yields of 1–8%. By contrast, MEG showed similar reactivity to methanol, producing bis(2-methoxyethyl) carbonate (BMEC) in yield of 29.6%. As listed in Table 2, the reactivity of the alcohol was found to decrease with increasing chain length of the alcohol. For instance, the yield of corresponding DAC was reduced from 28.1% to 1.1% when methanol was replaced by 1-butanol. This is rather surprising because the difference in pK_a value between methanol and 1-butanol is only 0.6 [38,39]. Most notably, the activity of K₂SeO₃ was completely quenched in 2-chloroethanol (pK_a = 14.3), 2,2,2-trifluoroethanol (pK_a = 12.5), and phenol (pK_a = 9.9) bearing an electron-withdrawing functional group [39]. These results suggest that the reactivity of an alcohol could be closely related to the pK_a value (or nucleophilicity) and the size of the alcohol employed. In other word, the carbonylation of an alcohol is strongly affected by both electronic and steric properties of the alcohol. Taken all these together, it is cautiously concluded that only moderately

nucleophilic alcohols bearing an electron-donating functional group and having a pK_a value of 15 ± 0.5 are highly reactive towards oxidative carbonylation, producing corresponding dialkyl carbonates in yields of 20–30%.

As hoped, malodorous dialkyl diselenides were not produced in the oxidative carbonylation of MEG conducted in the presence of K₂SeO₃ or Na₂SeO₃ at temperature up to 100 °C. In addition, the formation of RSeCO₂R and (ROSe)₂ (R = CH₃OCH₂CH₂) was not observed either. It is worth mentioning here again that the oxidative carbonylation of methanol using K₂SeO₃ produces CH₃SeCO₂CH₃ and (CH₃OSe)₂ along with (CH₃Se)₂. Se-containing organic by-products were not observed either from the oxidative carbonylation of ethanol, 1-propanol, and 1-butanol. The reason is not clear, but it is likely that the formation of Se-containing organic by-products from the carbonylation of methanol is attributed to the methylation of inorganic or organic selenium species by DMC. The routes to the formation of by-products in the oxidative carbonylation of methanol are proposed in Scheme S-1 (Supplementary Information). DMC is known to be an effective methylating agent, whereas the alkylating abilities of other dialkyl carbonates seem to be too weak to alkylate selenium species. This is probably the reason for the absence of Se-containing organic by-products from the oxidative carbonylation of alcohols other than methanol. Like the case in the oxidative carbonylation of methanol, the yield of BMEC using Cu-based catalysts was almost negligible under the same experimental condition (entry 11 and 12 in Table 2).

One significant advantage of preparing BMEC over DMC is that the oxidative carbonylation of MEG does not produce Se-containing volatile organic species, which are frequently observed in the carbonylation of methanol. The absence of Se-containing organic by-products can be largely attributed to the reduced alkylating ability of BMEC.

3.4. Effect of reaction temperature

The effect of temperature on the oxidative carbonylation of MEG and methanol was investigated using K₂SeO₃ as the catalyst. The molar ratio of MEG/catalyst was set at 30. As can be seen in Fig. 5, the yield of BMEC increased with the temperature rise up to 70 °C and then remained almost constant up to 100 °C. However, at temperatures above 100 °C, the BMEC yield decreased gradually. It seems that the hydrolysis of BMEC into MEG and CO₂ becomes favored at higher temperatures. Furthermore, the formation of Se-containing species seems to be facilitated at temperatures above 100 °C. Indeed, when the oxidative

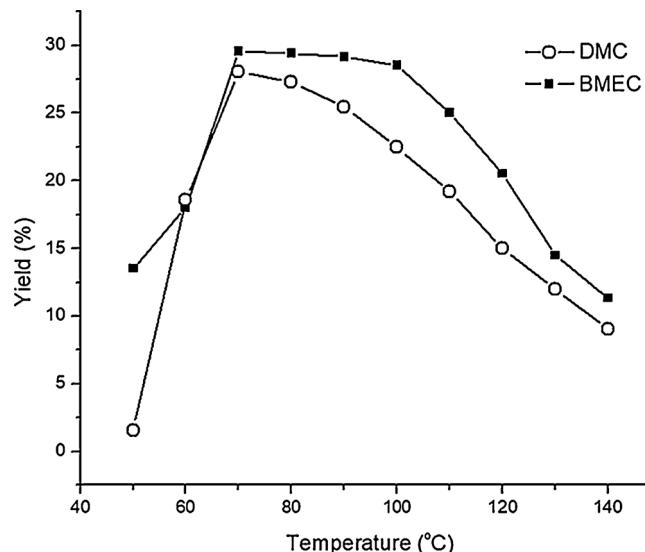


Fig. 5. Effect of temperature on the K₂SeO₃-catalyzed oxidative carbonylation of methanol and MEG to synthesize DMC (○) and BMEC (■), respectively.

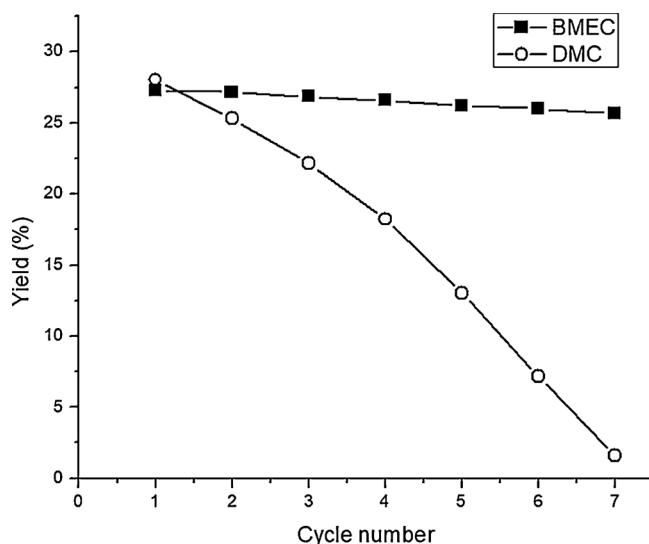


Fig. 6. Catalyst recyclability for the synthesis of DMC (○) and BMEC (■) from the oxidative carbonylation reactions of methanol and MEG, respectively, in the presence of K_2SeO_3 .

carbonylation of MEG conducted in the temperature range from 50 to 160 °C, any noticeable by-product was not observed up to 100 °C by GC and GC-Mass analysis (Supplementary Information, Fig. S-7 and S-8). However, above 100 °C, the yield and selectivity of BMEC started to decrease steeply with the temperature rise (Supplementary Information, Table S-1 and Fig. S-6). Like in the case of the carbonylation of methanol, a series of Se-containing by-products were produced (Supplementary Information, Table S-2). A similar trend was also observed in the synthesis of DMC, but the yield of DMC started to reduce very rapidly at above 70 °C, possibly due to the increased formation of organic selenium-containing by-products with the temperature rise.

3.5. Catalyst recyclability

To test the recyclability of selenite catalyst, oxidative carbonylation reactions were performed with MEG for 2 h at 70 °C and 5 MPa of CO/O_2 ($\text{vO}_2/\text{vCO} = 1/4$) using K_2SeO_3 as the catalyst. After a reaction period of 2 h, the liquid product mixture was removed by filtration using a cannula filter, and the remaining solid precipitates were washed with MEG, filtered again, dried under vacuum, and reused for further reactions with a fresh charge of MEG. As shown in Fig. 6, the catalyst retained most of its initial activity even after seven runs, suggesting that the catalyst is recyclable. This clearly indicates that most of active species are present in a heterogeneous state. In addition, XRD analysis of the solid precipitates recovered from the carbonylation of MEG conducted at 70 °C in the presence of K_2SeO_3 is also a mixture of elemental selenium and KHCO_3 (Supplementary Information, Fig. S-5). The selenium contents in the solids recovered after the first and seven cycles were measured by atomic absorption spectroscopic analysis (AAS) to determine the amount of selenium lost by leaching. It was assumed that K_2SeO_3 was converted into elemental Se and KHCO_3 , and the solubility of KHCO_3 in MEG was negligible. As can be conceivable from the result of the recycling test, the Se content was reduced only by 2.4% and 2.9% points from 38.5% (fresh) to 36.1% (after the fifth cycle) and 35.6% (after the seventh cycle), respectively, supporting that almost all the selenium species exist in a heterogeneous state under the experimental condition. However, the analysis of selenium content by AAS seems to be too complicated and time-consuming. In an attempt to simplify the analysis process for the determination of the selenium content, the amount of alcohol-soluble selenium species was analyzed by ^1H NMR spectroscopy. ^1H NMR spectrum of the liquid product mixture after the seventh cycle clearly shows that the formation of

MEG-soluble selenium-containing species from the carbonylation reactions at 70 °C with K_2SeO_3 is negligible (Supplementary Information, Fig. S-2).

Recyclability of the K_2SeO_3 was also investigated with methanol. Like the oxidative carbonylation of MEG, only the insoluble solid recovered from each cycle was reused for the next run. As shown in Fig. 6, the yield of DMC decreased gradually with the cycle. After seven cycles, DMC yield was reduced from 28.1% to 1.6%. The extent of selenium leaching from the oxidative carbonylation of methanol was also determined by NMR spectroscopy. As can be seen in Table R2, DMC yield was found to reduce from 28.1% to 1.6% after 7 cycles. Accordingly, the amount of methanol-soluble selenium species was increased up to 97.6 mol% after 7 cycles (Supplementary Information, Table S-4). The reason for the rapid decrease in DMC yield can be ascribed to the formation of methanol-soluble selenium species including $(\text{CH}_3\text{Se})_2$, $\text{CH}_3\text{SeCO}_2\text{CH}_3$, and $(\text{CH}_3\text{OSe})_2$ (Fig. 4), thus depleting the amount of catalytically active selenium species with each cycle.

3.6. Particle size and catalytic activity

As mentioned earlier, XRD and FT-IR analysis of the spent catalyst clearly showed that K_2SeO_3 was completely transformed into elemental Se and KHCO_3 (molar ratio of Se/ $\text{KHCO}_3 = 1/2$) (see Fig. 1) during the carbonylation reaction. As listed in Table 2 (entry 9), the mixed catalytic system composed of Se and KHCO_3 in a 1:2 molar ratio exhibited comparable activity to that of K_2SeO_3 in the oxidative carbonylation of MEG. The BMEC yield of 27.9% with the mixed catalytic system was close to that achieved in the presence of K_2SeO_3 (BMEC yield: 29.6%). However, in the oxidative carbonylation of methanol, the mixed catalyst exhibited much lower activity than K_2SeO_3 . The yield of DMC obtained with the mixed catalyst was almost two times less than that attained in the presence of K_2SeO_3 (14.4% vs 28.1%). There could be several reasons for higher activity of K_2SeO_3 than that of the mixed catalyst. As Se and KHCO_3 are found to be indispensable catalyst components, the rate of the carbonylation is likely to be affected by the particle sizes of both Se and KHCO_3 . The particle sizes of Se and KHCO_3 generated from the transformation of K_2SeO_3 during the oxidative carbonylation would be smaller than those of reagent grade Se and KHCO_3 , and thus K_2SeO_3 exhibit higher activity than the mixed catalyst because smaller sized Se and KHCO_3 derived from K_2SeO_3 would interact more strongly with a reaction mixture than reagent grade chemicals. This is probably one of the reasons for higher activity of K_2SeO_3 than the mixed catalyst comprising Se and KHCO_3 in the carbonylation of methanol. This is somewhat supported by the carbonylation reactions of methanol and MEG in the presence of a mixed catalyst. When the mixed catalyst was ground before use, the yields of DMC and BMEC were increased from 14.4% and 27.9% to 16.9% and 32.4%, respectively (see entries 9 and 10 in Table 1, and entries 9 and 10 in Table 2).

Interestingly, the yield of DMC was found to increase gradually to 27.1% after 6 h of the oxidative carbonylation of methanol in the presence of a mixed catalyst composed of Se and KHCO_3 in a 1:2 molar ratio. In contrast, the DMC yield was increased steeply up to 26.7% within 2 h and then remained almost constant on further progress of the reaction (Supplementary Information, Table S-3). It seems that the particle sizes of the mixed catalyst (Se/ KHCO_3) gets smaller with the time, thereby accelerating the reaction with the progress of the carbonylation reaction. This is probably an indirect evidence that the lower activity of the mixed catalyst than that of K_2SeO_3 is closely related to the larger particle sizes of Se and/or KHCO_3 .

Meanwhile, the comparable activity of the mixed catalyst (Se/ KHCO_3) to that of K_2SeO_3 for the carbonylation of MEG could be explained by assuming that MEG interacts more strongly with KHCO_3 than methanol, possibly due to its stronger acidity as well as to the presence of an additional oxygen atom, thereby facilitating the reduction of particle sizes of KHCO_3 and Se. Apparently, KHCO_3 seems to be better dispersed in MEG than in methanol (Supplementary Information,

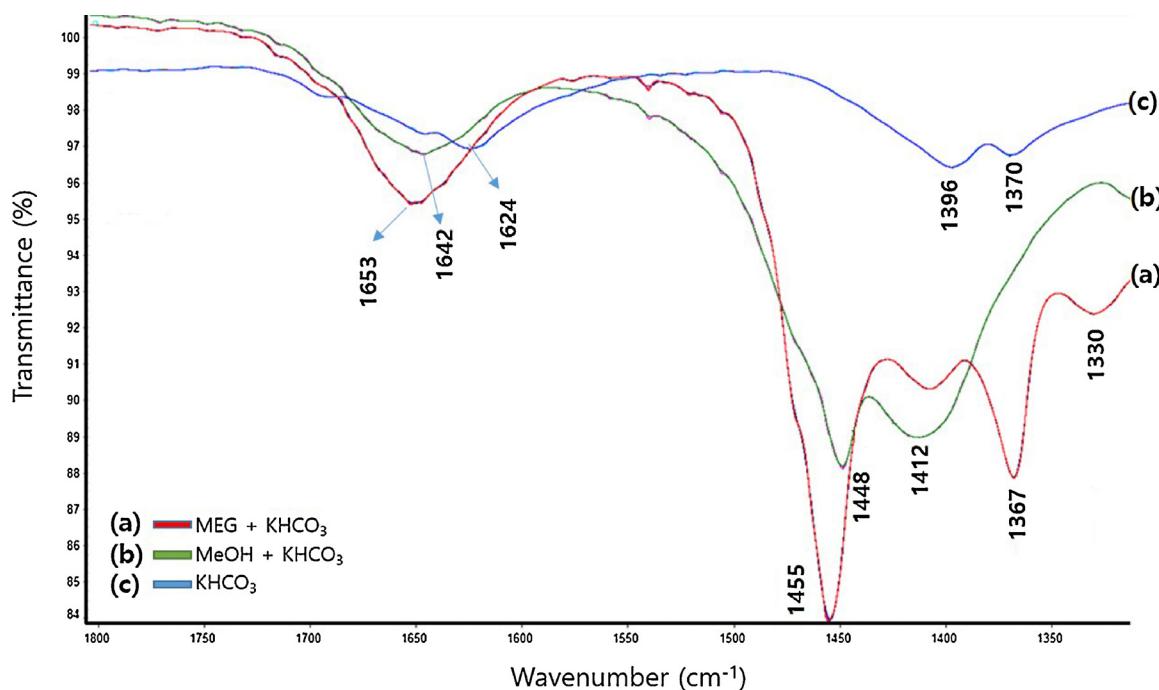
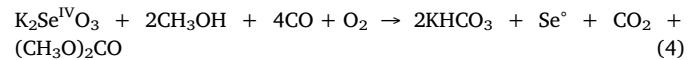


Fig. 7. FT-IR spectra showing the interactions of KHCO_3 with MEG and methanol, respectively: (a) MEG + KHCO_3 , (b) methanol + KHCO_3 , (c) KHCO_3 .

Fig. S-9). The interactions of KHCO_3 with MEG and methanol were compared by FT-IR spectroscopy. As shown in Fig. 7, the carbonyl peak of KHCO_3 at 1624 cm^{-1} was moved to a higher frequency by 29 cm^{-1} to 1653 cm^{-1} when mixed with MEG. The carbonyl absorption peak was also shifted to a higher frequency at 1642 cm^{-1} when mixed with methanol, but to a less extent by 18 cm^{-1} , indicating that MEG interacts with KHCO_3 more strongly than methanol. To have a better understanding of the activity difference between K_2SeO_3 and the mixed catalyst, particle sizes of the catalyst mixtures recovered from the carbonylation of methanol for 30 min were compared by scanning electron microscope (SEM). As expected, the particle sizes of the catalyst mixture derived from K_2SeO_3 were much smaller than those of the mixed catalyst composed of Se and KHCO_3 , supporting that the higher activity of the K_2SeO_3 can be attributed to the formation of smaller sized particles (Supplementary Information, Fig. S-11).

3.7. Mechanistic consideration

In consideration of XRD data, activity, and recyclability results, it is likely that the active species is Se (0), and the KHCO_3 plays a role as a promoter. This is reasonable because the catalytic role of Se (0) has been demonstrated in various other carbonylation reactions [33–35]. However, as shown in Table 1, elemental selenium was found to be completely inactive unless KHCO_3 was co-present. KHCO_3 was also inactive without the co-presence of Se (entries 13 and 14). The formation of elemental selenium from K_2SeO_3 is a strong indication that the reduction of Se (IV) to Se (0) is a facile process under oxidative carbonylation conditions. In a previous paper on the oxidative carbonylation of aromatic amines [36], we have shown by computational calculation that $[\text{Se}^{\text{IV}}\text{O}_2(\text{OCH}_3)]^-$ can be easily reduced by CO to give $[\text{Se}^{\text{II}}\text{O}(\text{OCH}_3)]^-$. The formation of CO_2 was confirmed by FT-IR spectroscopy. Therefore, further reduction of $[\text{Se}^{\text{II}}\text{O}(\text{OCH}_3)]^-$ by CO to elemental selenium can also reasonably be expected to occur without much difficulty unless a strong nucleophile like an amine or a phosphine is present to stabilize the $\text{Se}(\text{II})$ species. The co-production of KHCO_3 during the reduction of Se (IV) to Se (0) seems to be the result of the reaction of K_2SeO_3 with CH_3OH , CO, and O_2 as shown in equation (4).

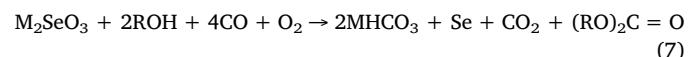
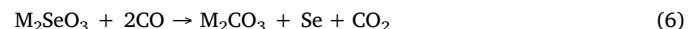


Although KHCO_3 is a weak base with a pK_b value of 7.65 [41], it could play a role in enhancing the nucleophilicity of MEG through a hydrogen bonding interaction, thereby facilitating the interaction of MEG with Se (0) species like carbonyl selenide ($\text{Se}-\text{CO}$).

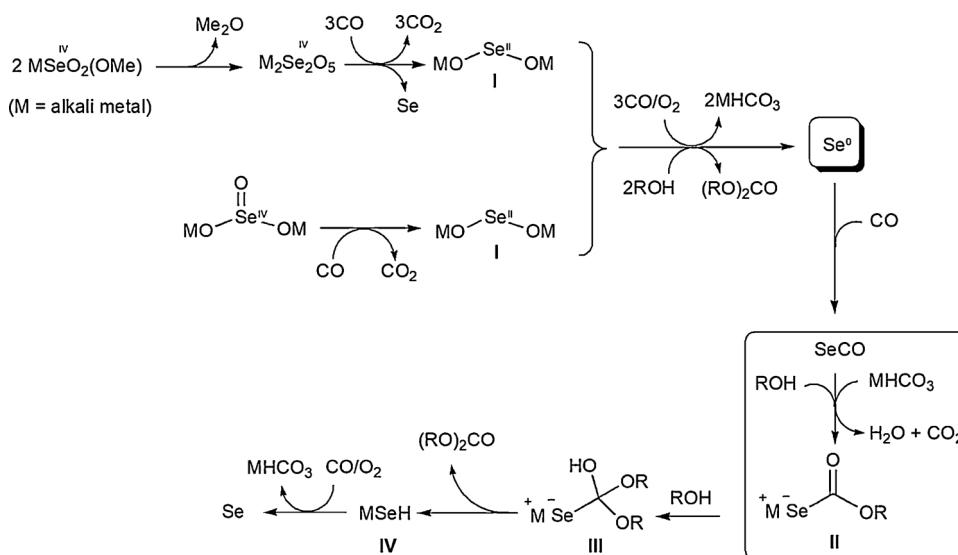
On the basis of the above discussion, a plausible mechanism for the carbonylation of MEG in the presence of $\text{MSeO}_2(\text{OMe})$ or M_2SeO_3 is suggested in Scheme 1. In a previous article, we have shown by X-ray crystallography that $[\text{BMIm}]\text{SeO}_2(\text{OMe})$ ($[\text{BMIm}]$: 1-butyl-3-methylimidazolium) can be transformed into $[\text{BMIm}]_2\text{Se}_2\text{O}_5$ by losing dimethyl ether (Me_2O) as shown in Eq. (5) [35].



Likewise, it is conceivable that $\text{MSeO}_2(\text{OMe})$ can be converted into $\text{M}_2\text{Se}_2\text{O}_5$ [42]. Subsequent reduction by CO would generate Se and an intermediate species, M_2SeO_2 (I), which is the same intermediate species generated from the reduction of M_2SeO_3 . The first step of the carbonylation would be the sequential reduction of $\text{M}_2\text{Se}^{\text{IV}}\text{O}_3$ by CO to elemental Se (0) via the formation of species I. During the reduction of $\text{M}_2\text{Se}^{\text{IV}}\text{O}_3$, M_2CO_3 (Eq. (6)) or MHCO_3 (Eq. (7)) can be co-produced.



However, it seems more reasonable to assume that MHCO_3 is produced directly from the reduction of M_2SeO_3 because no trace of M_2CO_3 is observed in the XRD patterns of the recovered catalyst after oxidative carbonylation of MEG. Moreover, the yield of DMC was reduced from 14.4 to 7.3% when Se/ MHCO_3 was replaced by Se/ M_2CO_3 when M is K (entries 9 and 11 in Table 1). Once produced, elemental selenium would react with CO to generate carbonyl selenide ($\text{Se}-\text{CO}$), which in turn interacts with MEG and MHCO_3 to afford MSeCO_2R (II, R = $\text{CH}_3\text{OCH}_2\text{CH}_2\text{R}'$) together with the formation of CO_2 and H_2O . Such a nucleophilic attack of MEG on the carbon atom of the carbonyl selenide can be attributed to a weak $\pi-\pi$ interaction existed in carbonyl selenide species, and the hydrogen bond interaction between an oxygen atom of



Scheme 1. A plausible mechanism of the synthesis of dialkyl carbonates from the MSeO₂(OMe) and M₂SeO₃-catalyzed oxidative carbonylation of alcohols.

KHCO₃ and the hydrogen atom of MEG. As mentioned earlier (Section 3.6.), FT-IR spectra in Fig. 7 clearly indicated that MEG interacts with KHCO₃ more strongly than methanol. Therefore, MSe(CO₂R) (II) can be regarded as a key intermediate for the formation of DACs in the catalytic cycle, and the facile interaction of MHCO₃ with MEG plays a critical role in the formation of intermediate II. The following reaction of the species II with another molecule of MEG would generate intermediate species III, which is immediately transformed into MSeH (species IV) and BMEC. The interaction of MSeH with CO/O₂ would generate elemental selenium and MHCO₃. The mechanism involving the formation of diselenides such as H₂Se₂ and R₂Se₂ (R = CH₂CH₂OCH₃) are not considered because they are not detected by NMR and Gas chromatography (Supplementary Information, Fig. S-1 and S-2).

4. Conclusions

Oxidative carbonylation reactions of alcohols were conducted in the presence of M₂SeO₃ or MSeO₂(OCH₃) (M: Li, Na, K, and Cs) to produce dialkyl carbonates. Among various alcohols tested, it was discovered that both methanol and MEG afforded corresponding dialkyl carbonates, DMC and BMEC in much higher yields (up to 32.8%) than those obtained using copper catalysts under the same conditions, while alcohols with electron withdrawing moieties such as F or Cl were found to be inactive. XRD analysis of the spent catalysts revealed that both M₂SeO₃ or MSeO₂(OCH₃) were transformed into elemental selenium and MHCO₃ during the course of the reaction, however, the MHCO₃ / Se residue formed in this reaction remained catalytically active for several subsequent reactions, suggesting that selenite is not necessarily the catalytically active species in this reaction. In the synthesis of DMC from the oxidative carbonylation of methanol, Se-based catalysts possess several advantages over Cu-based ones in terms of corrosiveness and activities. However, one considerable disadvantage in the use of Se-based catalysts was that a number of Se-containing volatile and methanol-soluble compounds including dimethyl diselenide, 1,2-dimethoxydiselenane, and O,Se-dimethyl carbonoselenoate were generated during the reaction. In contrast, BMEC was synthesized from MEG with high yield and high selectivity without producing volatile Se-containing by-products. BMEC is a high boiling aprotic polar compound and can be used as an alternative to DMC in secondary batteries. BMEC can also find uses as an alkoxy carbonylating agent in the synthesis of urethanes, intermediates of isocyanates.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2018.10.026>.

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